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# Iridium/Iridium Silicide as an Oxidation Resistant Capping Layer for Soft X-ray Mirrors

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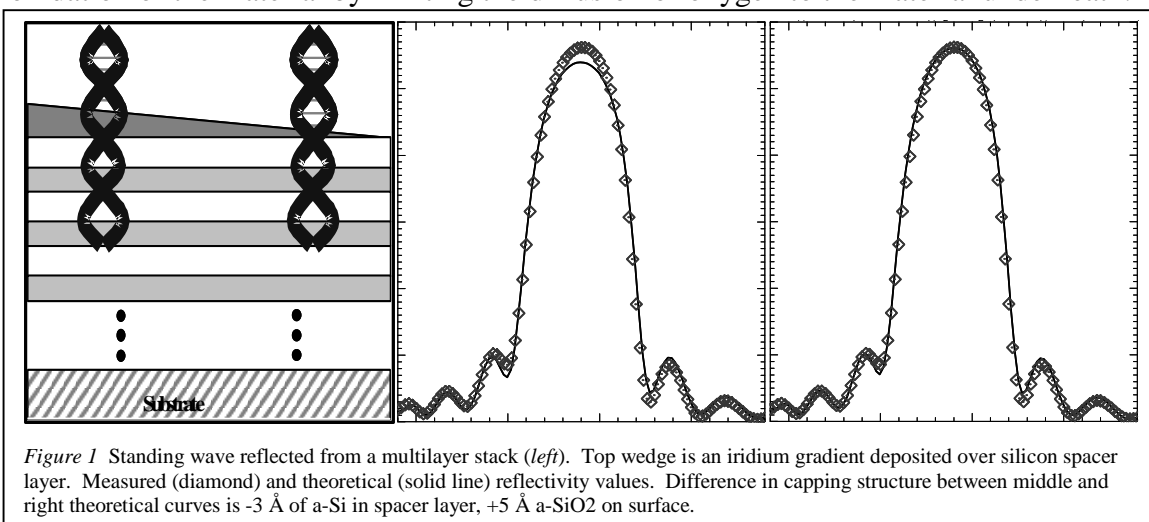
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## Introduction

Rust on a sword, tarnish on the silverware, and a loss in reflectivity for soft x-ray mirrors are all caused by oxidation that changes the desired characteristics of a material. Methods to prevent the oxidation have varied over the centuries with the default method of a protective coating being the most common. The protective coating for x-ray mirrors is usually a self-limiting oxidized layer on the surface of the material that stops further oxidation of the material by limiting the diffusion of oxygen to the material underneath.



The oxidation of an iridium on silicon capping layer was measured. A uniform molybdenum (Mo)/silicon (Si) multilayer stack was used to create a reflected standing wave of 13.4 nm light (see figure 1). A Si spacer and iridium (Ir) gradient were deposited on the uniform multilayer stack. The Ir gradient allowed for a range of Ir thickness ( $d_{Ir}$ ) values to be measured. Atomic force microscopy (AFM), energy dispersive x-ray spectroscopy (EDS), sputtering auger electron spectroscopy (SAES) and grazing angle x-ray diffraction (GAXRD) were used to measure the surface roughness, contamination of the deposited iridium, and depth profiles. The short wavelength of the light reflected from the Mo/Si stack makes for an excellent probe into the chemical makeup of the capping layer structure. The reflectance curve is extremely sensitive to the presence of oxygen and the relative amounts of silicon, molybdenum, and iridium (figure 1). After deposition, the capped structure was exposed to air and measured periodically

with 13.4 nm light to determine stability and elemental composition of the near surface region for signs of possible oxidation.

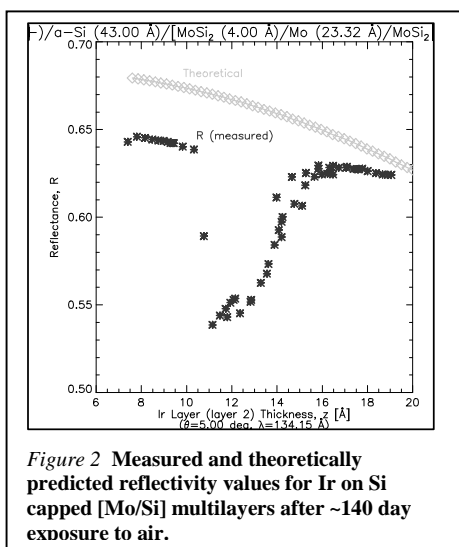
### Experimental

Deposition rates were determined using a series of Mo/Si bi-layer stacks and by changing the exposure time to the Mo and Si targets for each stack. DC magnetron sputtering was used to deposit the multilayers and exposure times used to control the actual thickness of the Mo and Si. Uniformity in reflectance of > 99.6% across the middle 80 mm of the 100 mm wafer was achieved.

To check the chemical composition of the iridium film EDS was performed on a thick iridium film grown on a Si wafer. 5 keV and 10 keV electron beam voltages were used but only iridium and silicon peaks were present in the resulting spectra.

Transit time over the Ir target was controlled to make graded iridium capping layers with iridium thickness ( $d_{Ir}$ ) values between 8 Å and 20 Å. Different transit times were matched to actual iridium gradients by: doing multiple passes over the iridium target with a bare silicon substrate wafer, measuring the resulting Ir thickness at seven points ( $r = 0, 12.5, 25, 37.5$  mm) along a diameter of the wafer by GAXRD, fitting of the GAXRD curves with IMD<sup>\*</sup>, assuming radial symmetry due to the high angular speed of the spinning substrate in relation to its linear velocity across the iridium target, and finally by fitting a second order equation with a least squares fit through the determined thickness values for each iridium profile and dividing by the number of passes made over the iridium target. A series of iridium capped multilayers were grown that covered the range of iridium thickness values  $7.5 \text{ Å} < d_{Ir} < 20 \text{ Å}$ . The reflectivity values of the capped multilayer structures were measured at beamline 6.3.2 at the Advanced Light Source and were used to evaluate the effectiveness of the capping layer.

### Results and discussion



A comparison between measured and theoretically predicted reflectivity values were made (figure 2). The model used to predict the reflectivity values assumed that the iridium film was on top of a silicon spacer layer and that an Ir to Si gradient formed at the Ir-Si interface. The measured reflectance curves were used to determine the thickness of the Ir gradient layer, the amount of SiO<sub>2</sub> formed, and the ability of the capping layer to stop oxidation over time. The [Ir/Si] capped multilayers were measured for stability over time for up to ~140 days. Between reflectivity measurements the multilayers were stored in air in standard 100 mm wafer Flouroware containers. It was determined from the time stability measurements that multilayers that

\* Software modeling package by David L. Windt that utilizes atomic absorption factors and density to help model the interactions between electromagnetic waves and matter. Freely available at <http://cletus.phys.columbia.edu/windt/idl>

were capped with a silicon spacer layer and  $16 \text{ \AA} < d_{\text{Ir}} < 20 \text{ \AA}$  or  $8 \text{ \AA} < d_{\text{Ir}} < \sim 10 \text{ \AA}$  were stable upon exposure to air.

The dip in reflectivity for  $\sim 10 \text{ \AA} < d_{\text{Ir}} < \sim 15 \text{ \AA}$  was unexpected and was further investigated. AFM was used to measure samples with  $d_{\text{Ir}} = 9.5, 10.6, 11.2, 18 \text{ \AA}$  (see figure 3) and a second sample was grown and measured to confirm the drop in reflectivity. The reflectivity curves generated at the ALS were carefully analyzed and modeled. SAES was performed on each side and in the middle of the dip ( $d_{\text{Ir}} = 9.5, 10.6, 11.2, \text{ and } 18.7 \text{ \AA}$ ). It was found that the drop in reflectivity was accompanied by an increase in surface roughness ( $2.17 \text{ \AA} \rightarrow 4.59 \text{ \AA}$  RMS) coupled with an increase in the amount of  $\text{SiO}_x$  present in the surface region.

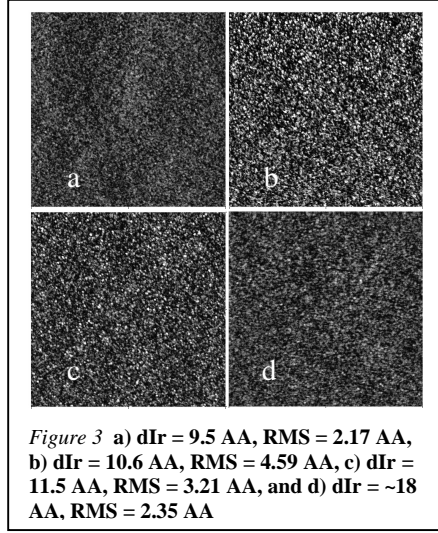
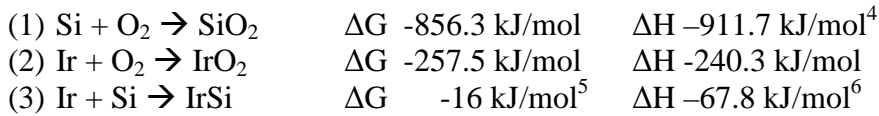


Figure 3 a)  $d_{\text{Ir}} = 9.5 \text{ \AA}$ , RMS = 2.17  $\text{\AA}$ , b)  $d_{\text{Ir}} = 10.6 \text{ \AA}$ , RMS = 4.59  $\text{\AA}$ , c)  $d_{\text{Ir}} = 11.5 \text{ \AA}$ , RMS = 3.21  $\text{\AA}$ , and d)  $d_{\text{Ir}} = \sim 18 \text{ \AA}$ , RMS = 2.35  $\text{\AA}$

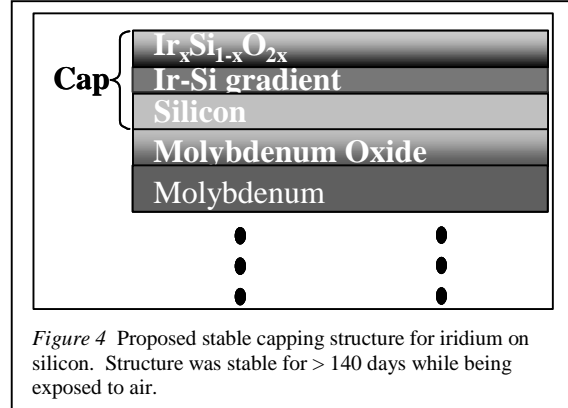
Modeling of the reflectance curves with IMD agreed with the presence of  $\text{SiO}_2$  on top of an Ir gradient as the cause for the drop in reflectivity and that the effect of the increase in surface roughness was negligible ( $< 0.1 \%$ ). The drop in the reflectivity over time was also correlated to an increase in the  $\text{SiO}_2$  thickness on top of the Ir gradient and a decrease in the a-Si spacer layer under the Ir gradient. A similar model but with the  $\text{SiO}_2$  formation under the Ir gradient or with just a  $\text{SiO}_2$  and Ir layer could not be made to agree with known amounts of deposited Ir and a-Si and the ALS reflectance curves. It must be noted that the IMD software used for modeling the ALS reflectance curves uses density and atomic absorption factors in calculating reflectance curves. It is not sensitive to phase changes in a material unless the change in phase influences the density or the atomic make-up of the material. The data fits the model exceedingly well but does not explain how or why the  $\text{SiO}_2$  layer forms.

It is proposed that the IrSi layer undergoes a phase change from an amorphous Ir-Si gradient (a-IrSi) to at least a partially crystalline Ir-Si gradient (pc-IrSi) at  $d_{\text{Ir}} \sim 10.5 \text{ \AA}$ . The formation of the  $\text{SiO}_2$  is would then be due to the increased rate of vacancy diffusion through the pc-IrSi in comparison to the a-IrSi. Prior investigations into the oxidation of silicides at high temperatures have found that there is rapid  $\text{SiO}_2$  formation that is not attributable to oxygen diffusion and kinetics but is thermodynamically driven<sup>1,2,3</sup> and that the  $\text{SiO}_2$  layer is very rough if oxidation occurs in dry oxygen<sup>1</sup>. There are three chemical reactions that must be taken into account.



It is clear that any silicon at the surface of the IrSi will oxidize until the oxygen concentration at the IrSi- $\text{SiO}_2$  interface falls below or equals the equilibrium oxygen concentration needed for (1) to occur. The formation of  $\text{SiO}_2$  acts as a diffusion barrier to the oxygen that, in turn, reduces the oxygen concentration at the IrSi- $\text{SiO}_2$  interface<sup>7</sup>. The method for transporting the silicon to the IrSi- $\text{SiO}_2$  interface has been determined to be vacancy diffusion<sup>1,2</sup> and has an activation energy ( $E_A$ ) of 1.9 eV<sup>3</sup> in c-IrSi or pc-IrSi. The lack of Si in the IrSi at the IrSi- $\text{SiO}_2$  interface creates a  $\sim 1.3 \text{ eV}$  chemical potential.

The oxidation of the Si releases ~9.5 eV of energy. It is most likely that the energy released by (1) combined with creation of a chemical potential due to (3) allows for the transport of the Si through the c-IrSi. Since transport is by vacancy diffusion it would be expected that amorphous IrSi (a-IrSi) would have a much lower vacancy diffusion rate due to larger Si-Si distances than that of c-IrSi, similar to what is seen in the silicon system<sup>8</sup> which relies upon the same mechanism for silicon transport and that oxidation of the iridium could occur. The presence of an iridium rich layer on top of the pc-IrSi would act as an additional diffusion barrier to oxygen, reducing the amount of SiO<sub>2</sub> needed in order to lower the oxygen concentration. The oxidation of the Si underneath the iridium rich layer also inhibits the diffusion of Si into the Ir rich layer.<sup>9</sup> Si diffusion into the Ir rich film is also inhibited by the low diffusion rate,  $R(T)$ , since  $R(T) \propto \exp\{-E_A/k_B T\}$  which is approximately  $1 \times 10^{-32}$  at room temperature for this system. Thus, a capping layer structure like that proposed in figure 4 should be thermodynamically stable upon exposure to oxygen.



<sup>1</sup> H. Jiang, C.S. Petersson, M.A. Nicolet, "Thermal oxidation of transition metal silicides," *Thin Solid Films*, **140**, 115-129 (1986).

<sup>2</sup> S.L. Zhang, F.M. d'Heurle, "A note on the linear-parabolic law of gas formation," *Philosophical Magazine A*, **64**, 619-627 (1991).

<sup>3</sup> S. Petersson, J. Baglin, W. hammer, F. d'Heurle, T.S. Kuan, I. Ohdomari, J. de Sousa Pires, P. Tove, "Formation of iridium silicides from Ir thin films on Si substrates," *J. Appl. Phys.* **50**, 3357-3365 (1979).

<sup>4</sup> D.R. Lide (Editor-in-chief), *CRC Handbook of Chemistry and Physics*, 81<sup>st</sup> Edition, 2000-2001, CRC Press LLC (2000).

<sup>5</sup> C. Ballesteros, T. Rodriguez, J. Jimenez-Leube, M. Clement, "Polycrystalline interlayer formed by deposition of thin-film iridium on silicon," *J. Appl. Phys.* **77**, 5173-75 (1995).

<sup>6</sup> M. Ohring, *The Materials Science of Thin Films*, Academic Press Inc. (1992).

<sup>7</sup> R. Pretorius, W. Strydom, J.W. Mayer, C. Comrie, "<sup>31</sup>Si tracer studies of the oxidation of Si, CoSi<sub>2</sub>, and PtSi," *Phys. Rev. B* **22**, 1885-1891 (1980).

<sup>8</sup> I.J.M.M. Raaijmakers, K. Kim, "A comparison of the reaction of titanium with amorphous and monocrystalline silicon," *J. Appl. Physics*, **67**, 6255-6264 (1990).

<sup>9</sup> K.L. Saenger, A. Grill, T.M. Shaw, D.A. Neumayer, Chenting Lin, Y.Y. Wang, "Stability and oxidation behavior of Ir thin film electrodes on Si and SiO<sub>2</sub>," *Mat. Res. Soc. Symp. Proc.* **541**, 119-127 (1999).

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